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PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of: Jean-Pierre Dath et al.  
Serial Number: 09/206,216  
Filing Date: December 5, 1998  
Examiner: T. Nguyen  
Group Art Unit: 1764  
Title: PRODUCTION OF OLEFINS

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APPEAL BRIEF

This is an appeal from the decision by the Examiner in the final rejection dated October 31, 2003 rejecting claims 17-20 and 37-40. This application was the subject of an earlier appeal filed September 6, 2002 with an Appeal Brief filed on December 17, 2002, accompanied by the statutory fee of \$320. Accordingly, it is respectfully requested that the fee paid with the first Appeal Brief be applied to this Appeal Brief in accordance with MPEP §1208.02. This Appeal Brief is submitted in triplicate.

As explained below under the headings Status of Claims and Status of Amendments, the claims pending in this application at the time of the final rejection and the filing of the Notice of

Appeal were claims 17-20 and 37-44. An amendment under 37 CFR §1.116 is being filed concurrently with this Appeal Brief to place claim 17, originally dependent from claim 37, in independent form by incorporating the subject matter of claim 37, and claim 37 has accordingly been cancelled. Upon entry of the amendment under 37 CFR §1.116, the claims for consideration in this appeal will be claims 17-20 and claims 38-44. Claims 18 and 19 are dependent from claim 17 and claims 38-44 are dependent from independent claim 20.

#### **Real Party in Interest**

The real party in interest is Fina Research, S.A., a Belgium corporation, as recorded by the assignment dated February 24, 1999, and recorded in the Patent and Trademark Office on March 22, 1999, at Reel/Frame 9843/0236.

#### **Related Appeals and Interferences**

There are presently no appeals or interferences directly related to this appeal. However, commonly-assigned applications having the same inventive entity as, or a common inventor with this application and directed to catalytic cracking processes are the subjects of appeals as indicated below.

Application Serial No. 09/206,218; Notice of Appeal filed August 22, 2002

Application Serial No. 09/596,356; Notice of Appeal filed June 10, 2002

#### **Status of Claims**

The claims pending in this application upon filing of the Notice of Appeal were claims 17-20 and 37-44. Upon entry of the amendment under 37 CFR §1.116 as referred to above, claim 17 would be amended to incorporate the subject matter of original parent claim 37 in its entirety and claim 37 would be cancelled. Thus, the claims pending in this application for consideration on appeal are claims 17-20 and claims 38-44. Claims 17-20 and 38-44 are reproduced in Exhibit A.

### **Status of Amendments**

An amendment under 37 CFR §1.116 is being filed concurrently with this Appeal Brief. Since this amendment cancels original claim 37 and amends claim 17 to incorporate the subject matter of original claim 37 and place claim 17 in independent form, it is presumed the amendment will be entered.

### **Summary of the Invention**

The claims on appeal are directed to a process for the cracking of olefins in an olefin-rich feedstock having dienes removed, employing an MFI crystallate silicate catalyst having a silicon/aluminum atomic ratio of from 180-1,000 (page 14, second paragraph). The feedstock is supplied to the MFI crystallate silicate catalyst at an inlet temperature of 500-600° C. Other reaction conditions include an olefin partial pressure of 0.1-2 bars, and a space velocity (LHSV) of from 10-30 h<sup>-1</sup> (page 7, first paragraph). In one aspect of the invention, the cracking process is specific to propylene and the effluent from the cracking process has a higher propylene content than the feedstock. The feedstock is treated to remove dienes from the feedstock prior to the cracking operation by selective hydrogenation of the dienes (page 7, second paragraph). The preliminary diene hydrogenation procedure is carried out at an inlet temperature of 40-200° C and a pressure of 5-50 bars, preferably 20-30 bars. The space velocity of the feedstock during the diene hydrogenation procedure is within the range of 2-5 h<sup>-1</sup> (paragraph bridging pages 19 and 20). The maximum diene concentration is 0.1 wt.%.

The MFI catalyst employed in appellants' invention is of a particular crystalline structure type as established by the Structure Commission of the International Zeolite Association as referred to on page 1 of appellants' specification. As stated there, ZSM-5 and silicalite are MFI-type crystalline silicates. Attached hereto as Exhibit B is a copy of pages 1-12 and 89-93 from

the *Atlas of Zeolite Structure Types* by Meier et al, published by the Structure Commission of the International Zeolite Association in 1978. As indicated on page 93, ZSM-5 and silicalite (referred to in Footnote 1 by reference to Flanigen et al (1978)) are MFI structure types. While both ZSM-5 and silicalite share the same structure type, they are otherwise distinctly different molecular sieves. ZSM-5 is a zeolite. Silicalite is not a zeolite but instead is a silica polymorph. Attached hereto as Exhibit C is a copy of the Flanigen et al. article (Flanigen, E. M., et al, "Silicalite, a new hydrophobic crystalline silica molecular sieve," *Nature*, vol. 271, February 9, 1978) referenced in page 93 of Meier et al., which together with U. S. Patent No. 4,061,724, referenced in Appellants' specification at page 2, provides a description of silicalite.

The effect of minimizing the diene content of the feedstock, specifically by a preliminary hydrogenation procedure, is illustrated by Example 15, with results shown in Figure 7, and Comparative Example 4, with results shown in Figure 8 (pages 39 and 40). In each of Example 15 and Comparative Example 4, dealuminated silicalite, having a silicon/aluminum atomic ratio of 182 in Example 15 and 180 in Comparative Example 4, is employed in the olefin cracking procedure. In Example 15, the feedstock was a light crack naphtha containing 37 wt.% olefins which was pretreated in order to hydrogenate the dienes originally present. In Comparative Example 4, employing a catalyst from Example 4 (page 29), the silicalite catalyst had a silicon/aluminum atomic ratio of 180. The feedstock had not been subject to a preliminary hydrogenation procedure, and had a diene content of 0.5 wt.%. In Example 15 (reported in Figure 7), the inlet temperature was 557° C, and the space velocity (LHSV) was 25 h<sup>-1</sup>. In Comparative Example 4, the inlet temperature was 570° C and the LHSV was 27 h<sup>-1</sup>. As can be seen from an examination of Figure 7, the propylene yield, after the initial startup of the process remained relatively constant over the life of the process up to about 220 hours onstream. In contrast, as shown in Figure 8, Comparative

Example 4 which had a diene content of 0.5 produced a steeply declining propylene yield from an initial value of about 18 wt.% to about 6 wt.% after about 140 hours onstream.

As illustrated by the experimental work and as described in appellants' specification at page 40, the feedstock containing a relatively high diene content resulted in a substantial and rapid deactivation of the catalyst. However, by initially hydrogenating the feedstock to hydrogenate the diene content therein, the result was a prolonged period of catalyst stability of up to 220 hours onstream.

### **Prior Art**

The prior art relied upon in rejecting the claims includes the following:

EP 109060 to Colombo;

U.S. Patent No. 4,078,011 to Glockner et al; and

U.S. Patent No. 4,347,392 to Cosyns et al.

### **Issues**

The issues in this appeal are whether each of claims 17-20 and 38-44 is obvious under 35 U.S.C. §103 over EP 109060 to Colombo in view of Glockner or in view of Cosyns. It is noted that the final rejection refers to a rejection under 35 U.S.C. §102(b) as involving anticipation. However, it is believed clear that there is no issue of anticipation and that the issue should be one of obviousness based upon an alleged combination of prior art references. This is reinforced by the various comments in the final rejection specifically identifying claim limitations which are not found in any individual reference.

### **Grouping of Claims**

In the arguments presented in this Brief, all of the claims do not stand or fall together. In addition to arguments applicable to all of the claims, additional arguments are presented referring specifically to each of the claims 17 & 40, 20, 41 & 42, and 43 & 44.

### **Appellants' Arguments**

As acknowledged in the final rejection, the primary reference to Colombo does not address the subject of dienes in the feedstock and does not address any sort of procedure for the hydrogenation of dienes, or for that matter, for the hydrogenation of anything else. For the reasons advanced below, appellants would respectfully submit that the teachings of Colombo and Glockner et al. or Cosyns et al. cannot be selectively combined in order to arrive at appellants' invention without a hindsight reconstruction of the prior art references which can be made only with the benefit of appellants' disclosure. Further, even if one of ordinary skill in the art, were, after considering appellants' disclosure, to attempt to combine Colombo and Glockner et al. or Colombo and Cosyns et al., the result would not involve the selective hydrogenation of dienes in an olefin-rich stream to form at least one olefin as set forth in claim 20, or further to form a feedstock having a maximum diene concentration of 0.1 wt.% as called for in independent claim 17 and set forth in dependent claim 40, dependent from claim 20.

Turning first to the rejection based upon Colombo and Glockner, it is noted that the secondary reference, Glockner, does not disclose selective hydrogenation of a feedstock for purposes even remotely similar to those involved in Colombo or in appellants' process. As the Examiner acknowledges, Colombo does not disclose a process for cracking of a feedstock containing dienes and further, does not disclose a procedure involving the hydrogenation of dienes. The patent to Glockner discloses the hydrogenation of dienes, but the Glockner

procedure is not concerned in any respect with the hydrogenation of a feedstock to be applied to a cracking process of any nature. In fact, cracking is not even mentioned in Glockner except as a source of an alkylation feedstock. In Glockner, the hydrogenation procedure is carried out in order to arrive at an olefin stream to be used as the feed in an alkylation process. Thus, the purpose of hydrogenation as disclosed in Glockner is to arrive at mono-olefins suitable for alkylation. Clearly, there is nothing in Glockner which would lead one of ordinary skill in the art to consider the Glockner process for the hydrogenation of dienes in a feedstock to be applied to a cracking process of any sort.

The Final Rejection observes that the primary reference, Colombo, does not require the presence of dienes. However, the absence in Colombo of any reference to dienes clearly would not suggest to one of ordinary skill in the art a process for the hydrogenation of dienes. More to the point, however, is the fact that the patent to Colombo does not require the absence of dienes, and further, there is no disclosure in Colombo of a maximum diene content of 0.1 wt.% as called for in claim 17 and in dependent claim 40. Further, even if one of ordinary skill in the art, after considering appellants' disclosure, were to attempt to combine the teachings of Colombo and Glockner, the result would be to seek to avoid more than 1% dienes since this is what Glockner disclosed for its alkylation feedstock. The result would not be to arrive at a maximum diene content of 0.1 wt.% or 0.05 or 0.03 wt.% as called for in dependent claims 41 and 42, respectively.

Other than the reference at the top of page 6 to the Cosyns abstract as disclosing hydrogenating dienes containing olefins, the Final Rejection does not appear to discuss the secondary reference to Cosyns et al. and accordingly, offers no basis in the prior art for combining the teachings of Cosyns with Colombo. However, it is clear that the Cosyns

procedure is not directed to the treatment of a feedstream in an olefin cracking process, and in fact, there is nothing in Cosyns to suggest that the Cosyns procedure would be suitable for such a process. Cosyns is actually directed to the selective hydrogenation of di-olefins and acetylenes in feedstocks containing ethylene and/or propylene. Presumably, the objective in Cosyns is to arrive at such feedstocks useful in the production of polyethylene or polypropylene. Clearly, there is nothing in Cosyns which would suggest the application of the Cosyns process to the treatment of a feedstock in an olefin cracking process.

In summary, there is no basis supplied in the prior art references to combine the teachings of EP '060 and Glockner or Cosyns. Further, even if one of ordinary skill in the art after reading appellants' disclosure were to attempt to combine the reference teachings, the result would be to target a diene content of 1 wt.%. It is further noted that the Final Rejection acknowledges that the secondary references fail to disclose a maximum diene concentration of 0.1 wt.%. To the extent that the calculations at the bottom of page 5 of the Final Rejection depart from this acknowledgement in an attempt to show a diene concentration of 0.1 wt.%, appellants would respectfully submit that the mathematical analysis presented there is incorrect and simply ignores what is actually disclosed in Glockner. Glockner, in Table 2, reports on test runs carried out employing a feedstock of 60 vol.% isoprene and 40 vol.% normal hexane. The conversion figure which the Examiner selected in his mathematical calculation would result in a diene content well above the 0.1 wt.% level specified in appellants' claims. In this respect, it is noted that the mathematical treatment found at the bottom of page 5 ignores the fact of the diene content (60 vol.%) as well as the selectivity of 90.2%. It is evident that the diene content actually arrived at in the effluent at ten hours on stream would be approximately 6.15%, arrived at by calculating



the amount of isoprene actually converted.<sup>1</sup> Further, even if the selectivity corresponding to the 99.5% conversion were 100% instead of the actual reported value of 90.2%, the remaining diene content would still be well in excess of 0.1 wt.%.

It should not be inferred from the foregoing that appellants accept the rationale put forth in the Final Rejection to support the proposed combination of EP '060 and Glockner. The point is, however, that even if one follows exactly the Examiner's rationale purporting to show a low diene content in Glockner, the result is a diene content well in excess of the 0.1% level called for in appellants' claims 17 and 40.

With respect to the comments found on page 8 of the Final Rejection relative to claims 43 and 44, appellants would respectfully submit that the assumption made in these calculations (that the product would necessarily contain 22.7g of isobutene per 100g of reactant) is unwarranted in view of the disclosure actually contained in Table 4 of Colombo. It would appear that the conversion figure of 77.3 in Table 4 of Colombo is stated with respect to the product components for which the selectivity values are presented. No figures are given for the product yield of isobutene and there is no basis in Colombo to assume 22.7g of isobutene passed through the reactor without change. In fact, the isobutene employed in Example 25 of Colombo could well contain butadiene, since 1,3-butadiene has a boiling point of about -4.4° C, very close to the -6.9° C boiling point of isobutene. In this regard, it is noted that isobutene is derived by the fractionation of refinery gases (See the attached page 652 from Hawley's Condensed Chemical Dictionary, 12<sup>th</sup> Ed. Submitted as Exhibit D) and the close proximity in boiling points of 1,3-butadiene and isobutylene could well result in the isobutylene fraction also containing butadiene. However, even assuming that the calculations presented on page 8 of the Final

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<sup>1</sup>  $60\% - 60\% \times 0.995 \times 0.902 = 60\% - 53.85\% = 6.15\%$

Rejection are fairly based, it will be noted that the olefin content of the feedstock and the effluent still would not be within  $\pm 10$  wt.% of each other as set forth in claim 44. To the extent the observations and calculations presented on page 8 of the Final Rejection are intended to show lack of patentability of original claim 37 (now claim 17), it will be noted that this claim calls for a space velocity, LHSV, of from 10 to 30  $\text{hrs}^{-1}$ . Example 25, relied upon in the analysis set forth in page 8 of the Final Rejection, specifies that the space velocity is well below the range called for in claim 17.

The patent to Cosyns is directed to the selective hydrogenation of a  $\text{C}_2 - \text{C}_3$  hydrocarbon fraction. The Colombo reference is directed to the conversion of  $\text{C}_{4+}$  hydrocarbons, and thus there would be no reason for one of ordinary skill in the art to look to Cosyns, which involves the hydrogenation of hydrocarbons of lower molecular weight than those employed in Colombo. Further, even if the teachings of Colombo and Cosyns were to be combined, the result would be a diene concentration well in excess of the 0.1 wt.% value called for in appellants' claims 17 and 40. In this regard, Cosyns, in column 1, lines 32-38, makes reference to a steam cracking charge containing 1-2% propadiene.

As demonstrated by the foregoing remarks, it is respectfully submitted that the combinations of the secondary references, Glockner et al. or Cosyns et al. with Colombo as the primary reference cannot be made in a manner to arrive at appellants' invention, even if it were appropriate to use appellants' teachings as a basis for combining the diverse teachings of the references. This, however, is not the appropriate standard to be applied in combining prior art teachings. The appropriate standard forbids using an appellants' own disclosure as a basis for assembling prior art teachings and requires a suggestion or motivation in the prior art as reflected in decisions in *ACS Hospital Systems, Inc. v. Montefiore Hospital*, 221 USPQ 929 (Fed. Cir.

1984) and *Ex parte Giles* 228 USPQ 886 (PTO Bd. Of Appeal. And Int. 1985). As expressed by the Board in *Giles* at 688:

Only appellant's disclosure and not the prior art provides a motive for achieving the combination as claimed by the appellant. To imbue one of ordinary skill in the art with knowledge of the invention . . . when no prior art reference or references of record convey or suggests that knowledge is to fall victim to the insidious effect of a hindsight syndrome wherein that which only the inventor taught is used against its teacher.

Attention is also respectfully invited to the Federal Circuit decision in *In re Fine*, 5 USPQ2d 1956 (Fed. Cir. 1988) wherein the Court stated at 1600:

It is essential that "the decisionmaker forget what he or she has been taught at trial about the claimed invention and cast the mind back to the time the invention was made . . . to occupy the mind of one skilled in the art who is presented only with the references, and who is normally guided by the then-accepted wisdom in the art." *Id.* One cannot use hindsight reconstruction to pick and choose among isolated disclosures in the prior art to deprecate the claimed invention. (Emphasis added)

The admonitions in *Ex parte Giles* and *In re Fine* are to step back in time to evaluate the invention only in the context of what is disclosed in the references without regard to what is disclosed in appellants' specification. When this is done, it is believed clear that one of ordinary skill in the art would not arrive at appellants' invention based only upon the references and "the then-accepted wisdom in the art." It is only with the benefit of hindsight after a reading of appellants' disclosure, would it occur to one of ordinary skill in the art to attempt to combine Glockner et al., directed to alkylation feeds, or Cosyns et al., directed to polymerization feeds, with Colombo in an attempt to hydrogenate dienes, which are non-existent in Colombo, to arrive at an olefin cracking feedstock.

In regard to the reliance in the Final Rejection on the holding of *in re McLaughlin*, 443 F2d 1392, 170 USPQ 209 (CCPA 1971), the *McLaughlin* case which led to the conclusion of a *prima facie* case of obviousness in view of what the reference disclosures would suggest to one

of ordinary skill in the art, does not countenance hindsight reconstruction of the prior art of the type condemned in the decisions cited above. As noted previously, the various processes disclosed in Colombo, Glockner and Cosyns are so diverse and unrelated that the attempt to combine their teachings is based not on knowledge which was within the level of one of ordinary skill in the art, but on appellants' own disclosure. Further, as noted above, the combined teachings of the references fall short of appellants' claimed subject matter.

As further acknowledged in the Final Rejection, the Colombo reference fails to disclose the use of an MFI catalyst having a silicon/aluminum atomic ratio of 180-1,000 as required in appellants' claims. Instead, Colombo merely refers to a silicon/aluminum ratio of at least 175 with no upper limit, disclosing a catalyst in which no aluminum is present, *i.e.* a silicon/aluminum ratio of infinity. Thus, the teaching in Colombo is that the silicon/aluminum atomic ratio is of no significance and, in fact, that it makes no difference whether or not aluminum is even present in the catalyst. Appellants would respectfully submit that the Examiner is in error in suggesting that the disclosure of a very broad range would in itself render obvious a specific narrower range included within the broad range. Specifically, to the extent that the rejection relies upon the premise that the disclosure of very broad ranges encompassing narrow ranges amounts to a disclosure of such narrow ranges or renders the use of such ranges obvious, appellants would respectfully disagree. It is believed to be well established that the existence in the prior art of broad ranges which encompass narrow ranges presented in the claims does not in itself establish lack of novelty or obviousness of such ranges. In this regard, attention is respectfully invited to *In re Russell*, 169 USPQ 426, CCPA (1971) wherein the court in reversing the rejection of the claims stated:

Essentially, appellant's contention is that the employment of the proportions recited in the claims unexpectedly yields clear compositions without the need for a filtration step. Appellant's position on the law is sound, for even though part of appellant's range of proportions, and all of his ingredients, are

suggested by the broad teaching of Wei, if appellant can establish that his relatively narrow ranges yield unexpectedly superior results as against the broad Wei ranges as a whole, appellant will have established unobviousness of the claimed invention. See *In re Luvisi*, 51 CCPA 1063, 342 F.2d 102, 144 USPQ 646 (1965); *In re Neave*, 54 CCPA 999, 370 F.2d 961, 152 USPQ 274 (1967).

For a similar holding, reference is made to *In re Waymouth and Koury*, 182 USPQ 290, CCPA (1974). In this case, the claims on appeal were directed to a lamp having an arc tube containing halogen in mercury atoms present in a ratio of 0.08 to 0.75. The prior art reference disclosed a similar device containing halogen and mercury atoms. The calculated ratio of halogen to mercury atoms inherently disclosed in the reference ranged from 0.0000001 to 1.3. Although the prior art range enveloped the narrower range claimed by appellant, the court reversed the rejection of the claims in view of the unexpectedly superior results achieved by operating within the claimed range.

In the present case, similarly as in the *Russell* and *Waymouth* decisions, appellants' invention involves the use of the catalyst having characteristics which are not taught by the prior art and which produce unexpectedly superior results which are not recognized by the prior art references. Accordingly, appellants respectfully submit that the claims are patentable over the prior art references by virtue of the claimed silicon/aluminum atomic ratio of 180-1,000.

In addition to the requirement in claims 17 and 20 of a silicon/aluminum atomic ratio of 180-1,000, these claims require an inlet temperature of 500° to 600° C and claim 17 specifies a space velocity (LHSV) of 10 to 30 h<sup>-1</sup>. Claim 20 further recites an olefin partial pressure of from 0.1 to 2 bar. Colombo does not disclose or suggest this particular combination of parameters and instead discloses, in addition to the very broad range of the silicon/aluminum ratio, broad ranges of olefin partial pressure, space velocity, and temperature. Thus, Colombo specifies a temperature of 400° to 600° C, a space velocity of 5 to 200 h<sup>-1</sup>, and a pressure of 1.5 to 7.5 atmospheres. The only qualification on space velocity appears to be a space velocity of less than 50 h<sup>-1</sup> if the pressure is

atmospheric and greater than  $50 \text{ h}^{-1}$  at a pressure of from 1.5 to 7.5 atmospheres. In fact, with the single exception of Example 36, the space velocity in Colombo is well below the 10 to  $30 \text{ h}^{-1}$  range called for in claim 17 or well above this range as in Examples 32-35. In Example 36 of Colombo, the space velocity is  $20 \text{ h}^{-1}$ . However, Example 36 does not specify a silicon/aluminum atomic ratio within the range called for in appellants' claims, and the only inference that can be drawn from the reference disclosure is that this ratio, like the ratio of the other examples of silicalite -1 disclosed in the reference, is well above the upper limit of 1,000 called for in the claim. In this respect, every example of silicalite -1, as described in Colombo specifies that no aluminum is present.

Appellants respectfully disagree with the Examiner's position that data in Colombo indicates that the olefin contents of the feed and product are substantially the same by weight as set forth in claim 17. Nor are they within  $\pm 15\%$  of each other as set forth in claim 43 or with  $\pm 10 \text{ wt. \%}$  as recited in claim 44. Further, it is again noted that claim 17 requires, in addition, a temperature range of  $500^\circ - 600^\circ \text{ C}$  and a space velocity of 10 to  $30 \text{ h}^{-1}$ . As noted above, with the exception of Example 36, all of the space velocities shown in the various examples of Colombo are outside of the claimed range. As to relative olefin content of the feed and the effluent, there is no clear indication in the various examples that these values are within  $\pm 15\%$ . In some cases they are clearly outside of this range. For example, the products in Examples 16-23, which show high selectivity to BTX, clearly do not involve an effluent having an olefin content within 15% of the olefin content of the product stream. In other examples, it is impossible to determine whether the claimed relationship between the feed stream and the effluent stream is met. Similarly, Examples 1-6 show a very high product in the effluent of  $\text{C}_{5+}$  compounds. It is not clear whether these are saturated or unsaturated, and thus again, a determination as to the relevant olefin content of the feedstock and effluent cannot be made. In

any event, it will be recalled that whether or not these various examples involve an effluent and a feedstock having olefin contents within 15%, they clearly do not involve the space velocity requirements of claim 17. The sole example of Colombo, which does indicate a space velocity within appellants' claimed range, is Example 36, as noted above. Example 36 does not, however, disclose the relationship between the olefin contents of the feed and the effluent as claimed. Moreover, the disclosure in Example 36 of Colombo indicates that the relative olefin contents of the feed and effluent could be substantially different. In this respect, the olefin content of the feed in Example 36 is 100% normal butene whereas the identified olefin content of the effluent (propylene, ethylene, and isobutylene) is about 50%. About 4-5% of the effluent is identified as saturated gases, with the remainder being identified as C<sub>5+</sub> liquids. Presumably, substantial portions of these liquids would be olefins resulting from butene oligomers which are unsaturated. However, if as much as even 30% of the C<sub>5+</sub> liquids are saturated, it is clear that the olefin content of the effluent would not be within 15% of the olefin content of the feedstock.

As to the Examiner's alternative ground based upon inherency, appellants respectfully note that the law is well settled that for an alleged inherent feature to result from a prior art teaching, it is necessary that this inherent feature necessarily flow from the teachings of the prior art. Thus, an alleged inherent feature must be a necessary result and not merely a possible result. This principle is stated in MPEP Section 2112:

The fact that a certain result or characteristic may occur or be present in the prior art is not sufficient to establish the inherency of that result or characteristic. (Emphasis original)

Section 2112 reflects the general rule that for inherency to reside, it must be shown that the alleged inherency is necessarily present and not a mere possibility. Thus, as stated by the Board in *Ex parte Keith*, 154 USPQ 321 (Bd. of App. 1966), in reversing the Examiner's rejection based upon

inherency:

There are other possible courses the reaction could follow . . .  
Asserted inherency must be a necessary result and not merely a possible result.

As indicated in Section 2112, this principle was more recently followed by the Board in *Ex parte Levy*, 17 USPQ2d 1461 (Bd. of App. and Interf. 1990), where the Board reversed an inherency rejection, stating as follows:

In relying upon the theory of inherency, the examiner must provide a basis in fact and/or technical reasoning to reasonably support the determination that the alleged inherent characteristic necessarily flows from the teachings of the prior art (citing cases). (emphasis original).

Here, this claimed subject matter clearly is not inherent in Colombo.

### **Conclusion**

For the reasons set forth above, appellants respectfully submit that all of the claims herein are patentable over the prior art. Accordingly, it is respectfully requested that the Final Rejection of the claims be reversed.

The Commissioner is hereby authorized to charge the Locke Liddell & Sapp LLP Deposit Account No. 12-1781 for any fees due in connection with this communication.

Respectfully submitted,



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Date: May 3, 2004

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### **Exhibit A**

The claims on appeal are as follows:

17. A process for cracking an olefin-rich hydrocarbon feedstock which is selective towards propylene in the effluent, the process comprising contacting a hydrocarbon feedstock having a maximum diene concentrated therein of 0.1 wt.% containing olefins having a first composition of at least one olefinic component with an MFI crystalline silicate catalyst having a silicon/aluminum atomic ratio of from 180 to 1000 to produce an effluent having a second composition of at least one olefinic component, the feedstock contacting the catalyst at an inlet temperature of from 500 to 600° C and being passed over the catalyst at an LHSV of from 10 to 30h<sup>-1</sup>, the feedstock and the effluent having substantially the same olefinic content by weight therein, and the effluent having a higher propylene content than the feedstock, wherein the dienes have been removed from the feedstock prior to the cracking step by selective hydrogenation.

18. A process according to claim 17, wherein the diene hydrogenation process is carried out at an absolute pressure of from 20 to 30 bar and an inlet temperature of from 40 to 200° C.

19. A process according to claim 18, wherein the LHSV of the feedstock in the diene hydrogenation process is from 2 to 5h<sup>-1</sup>.

20. A process for the cracking of olefins in a hydrocarbon feedstock containing at least one diene and at least one olefin, the process comprising hydrogenating the at least one diene to form at least one olefin in the presence of a transition metal-based hydrogenation catalyst at an inlet temperature of from 40 to 200° C and an absolute pressure of from 5 to 50 bar with a hydrogen/diene molar ratio of at least 1, and catalytically cracking the olefins in the presence of an MFI crystalline silicate catalyst having a silicon/aluminum atomic ratio of from

180 to 1000 at an inlet temperature of from 500 to 600° C and an olefin partial pressure of from 0.1 to 2 bar to produce an effluent having at least one olefin and having a different olefin distribution with respect to average carbon number than the at least one olefin in the feedstock.

38. A process according to claim 20 wherein the LHSV of the feedstock in the diene hydrogenation process is from 2 to 5 h<sup>-1</sup>.

39. A process according to claim 38 wherein the diene hydrogenation process is carried out at an absolute pressure from 20 to 30 bars and an inlet temperature from 40 to 200° C.

40. A process according to claim 20 wherein said hydrogenation is carried out to provide a maximum diene concentration in said feedstock of 0.1 wt.%.

41. A process according to claim 40 wherein the maximum diene concentration is 0.05 wt.%.

42. A process according to claim 40 wherein the maximum diene concentration is 0.03 wt.%.

43. A process according to claim 20 wherein the olefin content of the feedstock and the olefin content of the effluent are within  $\pm 15$  wt.% of each other.

44. A process according to claim 43 wherein the olefin contents of the feedstock and the effluent are within  $\pm 10$  wt.% of each other.

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ATLAS OF ZEOLITE STRUCTURE TYPES

by  
W. M. MEIER and D. H. OLSON

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of the International Zeolite Association

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## PREFACE

The steadily growing number of known zeolite structures and numerous requests which have been received for a previous survey of zeolite framework types has led to the present "Atlas of Zeolite Structure Types". The primary aim of the present compilation is to define and to supply a condensed characterization of the 38 currently established zeolite structure types. Apart from the stereopairs illustrating the framework structures the Atlas contains summaries of structural data as well as a Structure Type Index that includes all natural and synthetic materials which have been shown to be an isotype of a known zeolite structure type.

The present Atlas contains only reasonably well-established structures which have been at least partially refined. A number of zeolite structures included are by necessity based on powder data. A total of 38 structure types could, after critical assessment of the respective structure analysis, be included in this Atlas (compared to 27 in the previous survey by Meier and Olson, 1971).

Zeolites do not comprise an easily definable family of crystalline aluminosilicates. The inclusion or exclusion of borderline cases was decided on the basis of criteria used at recent International Conferences on zeolites.

We wish to acknowledge the use of the stereographic computer plotting program ORTEP, written by Dr. Carroll K. Johnson (Oak Ridge National Laboratory). A listing of the ORTEP input used to generate the stereopairs in this Atlas has been deposited as document number NAPS-03331. (Order from ASIS/NAPS, Microfilm Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10017). Information obtained by private communication in addition to the published data has in several instances been used in the preparation of the Atlas. Such use is indicated in the References and we gratefully acknowledge this help. We also wish to thank our colleagues of the IZA Structure Commission for critically

reading the manuscript and many helpful comments. Furthermore, we are grateful for the support by Mobil Research and Development Corporation and one of us (D. H. O.) is also indebted to this company for permission to participate in this project. The work of the other author (W. M. M.) has been part of a research program supported by the Swiss National Science Foundation.

## Explanatory Notes

Probably the simplest way of illustrating zeolite structures is by means of skeletal models or diagrams showing the 4-connected nets formed by the tetrahedral atoms in the various aluminosilicate frameworks. The known zeolite framework types are presented in this Atlas by means of stereographic drawings of this kind. In general, the viewing direction (which is stated in each case) has been chosen in such a way that the main channels are clearly visible. The unit cell has also been outlined whenever possible and provided that no changes in symmetry affecting the cell edges have been encountered. The positions of T-atoms (T = Si, Al) are those of the points or vertices of the net and the T-O-T bridges are represented by straight lines. The positions of the O-atoms are only approximately displayed in these diagrams since the T-O-T angles are typically around 140-150°. The idealization makes it easier to visualize the topology and basic features of zeolite framework structures which in many instances are relatively complex.

## STRUCTURE TYPE

Structural classifications of zeolites are primarily based on the topology of the frameworks. Zeolite species which do not differ with respect to the framework topology are called isotypic, i.e. they have the same structure type irrespective of composition, distribution of the different T-atoms, cell dimensions, and symmetry. A mnemonic code consisting of 3 capital letters has been adopted for each structure type following the recommendations by IUPAC on zeolite nomenclature<sup>1)</sup>.

1) "Chemical Nomenclature, and Formulation of Compositions, of Synthetic and Natural Zeolites", prepared by a special IUPAC Commission under the chairmanship of R. M. Barrer. IUPAC yellow booklet, 1978.

structure type codes are generally derived from the names of the type species (see below) and do not include numbers and characters other than capital roman letters. Since structural criteria alone do not provide an unambiguous numbering scheme, and to facilitate later additions and simple indexing, the various structure types in this Atlas have been arranged in alphabetical order according to the structure type code. For each structure type the information given in bold type includes the full type name, the maximum topological symmetry (i.e. maximum possible space group) and a listing of the topologically distinct T-atoms, their number per unit cell, as well as the maximum point symmetry of the respective T-sites (in square parentheses).

#### secondary Building Units (SBU)

Zeolite frameworks can be thought to consist of finite or infinite (i.e. chain- or layer-like) component units. The finite units containing up to 16 T-atoms, which have been found to occur in framework silicates, are shown in Figure 1. These secondary building units<sup>1)</sup> are derived assuming the entire framework is made up of one type of SBU only<sup>2)</sup>. Each unit cell invariably contains an integral number of SBU. Many of the frameworks can be built from several different SBU. In these cases the SBU listed in the first place is the one which occurs most frequently in related structures.

1) The primary building units being the single  $\text{TO}_4$  tetrahedra.

2) There is evidence, however, that some zeolite frameworks consist of two component units, such as 4-membered rings of silica tetrahedra which are linked to each other through single  $\text{AlO}_4$  tetrahedra.

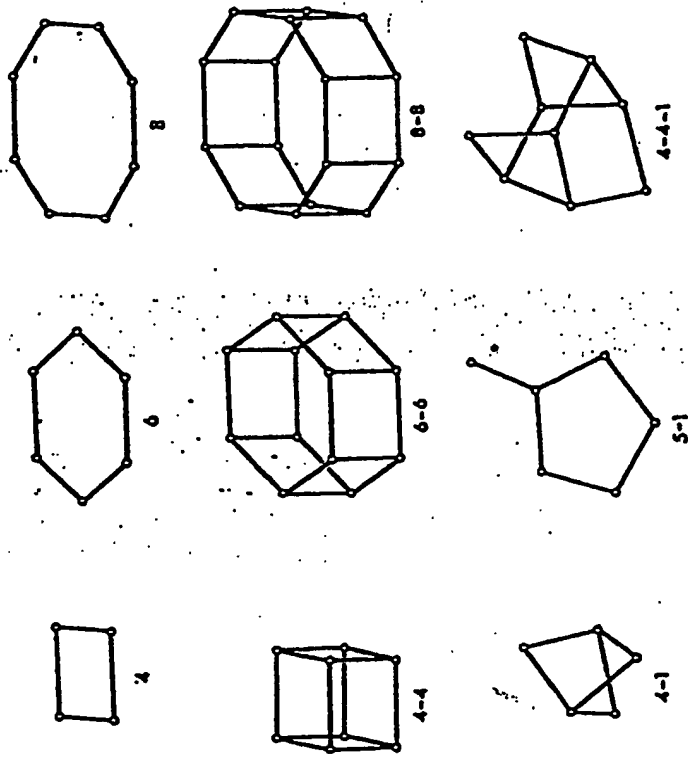


Figure 1

#### Framework Density (FD)

This is defined as the number of T-atoms per  $1000 \text{ \AA}^3$ . For zeolite frameworks structures values of at least  $20 \text{ T}/1000 \text{ \AA}^3$  are general. For structures with the largest pore volume to around 20. The FD is obviously related to the pore volume but does not reflect the size of the pore openings. For some non-rigid zeolite structure types the FD values can vary appreciably. In these cases (such as glauconite) values are given for the type species and the framework in the most expanded state. The flexibility of the framework structure is to some extent displayed by the possible variation of the FD.



hand notation has been adopted for the description of the channels of the various frameworks. Each system of equivalent channels is characterized by a number of either T- or O-atoms (underlined number) forming the smallest rings of the channels, and a crystallographic free diameter of the channels.

Free diameter values are based on the atomic coordinates of the apertures in the hydrated state and an oxygen radius of 1.35 Å. Minimum and maximum values are given for non-circular apertures. In instances the corresponding interatomic distance vectors are approximately co-planar, and closer inspection of the diagrams give some information on this in the first instance. It should be noted that crystallographic free diameters depend on the state of composition of the zeolite, and can differ appreciably for various zeolite species, particularly in the case of non-rigid frameworks.

Number of asterisks in the notation used indicates whether the channel system is one-, two- or three-dimensional. Only those apertures are taken into account which are more open than regular six-membered rings. In most cases these smaller openings simply form windows (rather than channels) connecting larger cavities. Interconnected channel systems are separated by a double arrow ( $\longleftrightarrow$ ). A vertical bar (|) means that there is no direct access from one channel to the other.

Selected examples in Table 1 illustrate the various possibilities in the use of the notation. Cancrinite is characterized by a one-dimensional system of channels parallel to  $[001]$  or  $c$  with circular apertures. In offretite the main channels form a similar system and are interconnected by channels made of 8-rings giving rise to a

3-dimensional channel system. The channel system in mordenite is essentially 2-dimensional, the 12-ring apertures of the main channels being somewhat elliptical. Paulingite is an example of a framework type containing two independent sets of 3-dimensional channel systems which are displaced against each other.  $\langle 100 \rangle$  means there are channels parallel to all crystallographically equivalent axes of the cubic structure, i.e. along  $x$ ,  $y$  and  $z$ . In gismondine the channels parallel to  $[100]$  together with those parallel to  $[010]$  give rise to a 3-dimensional channel system which can be pictured as an array of partially overlapping tubes.

Table 1: EXAMPLES ILLUSTRATING THE NOTATION FOR THE CRYSTALLOGRAPHIC CHARACTERIZATION OF THE CHANNEL

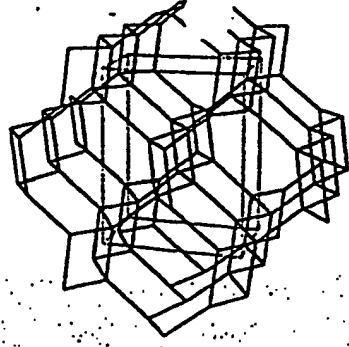
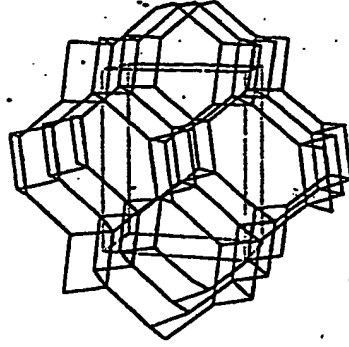
Cancrinite	$[001] \underline{12} \underline{6.2} *$
Offretite	$[001] \underline{12} \underline{6.4} * \longleftrightarrow \perp [001] \underline{8} \underline{3.6} \times \underline{5.2} **$
Mordenite	$[001] \underline{12} \underline{6.7} \times \underline{7.0} * \longleftrightarrow [010] \underline{8} \underline{2.9} \times \underline{5.7} *$
Paulingite	$\langle 100 \rangle \underline{8} \underline{3.9} *** \mid \langle 100 \rangle \underline{8} \underline{3.9} ***$
Gismondine	$\{ [100] \underline{8} \underline{3.1} \times \underline{4.4} \longleftrightarrow [010] \underline{8} \underline{2.8} \times \underline{4.9} \} ***$

#### Fault Planes (FP)

Likely FP are listed for each structure type. The existence of FP means that layer-like segments of the framework can be stacked in more than one way, giving rise to polytypism. A number of related structures (polytypes) can be readily postulated on this basis. FP also serve as an indication of possible stacking faults which may affect the critical channel dimensions.

# Type Species and References

The type species stated in the data section is the species used to establish the structure type. In the majority of cases these have been natural zeolites providing single crystal data. The composition expressed in terms of cell contents has in many cases been idealized inasmuch as compositional data give average unit cell contents which frequently correspond to fractional numbers of atoms. Isotypic species are very common and have been listed in the Index.



Li-A(BW)

Imam

8 T[m]

viewed along [001]

Secondary building units: single 4-rings  
(single 6- or 8-rings)

Framework density: 19.0 T/1000 Å<sup>3</sup>

Channels: [001] 8 3.6 x 4.0 \*

Fault planes: (010), (011)

Type species:

synthetic zeolite Li-A (Barrer + White)

Li<sub>4</sub>Al<sub>4</sub>Si<sub>4</sub>O<sub>16</sub> · 4 H<sub>2</sub>O

orthorhombic, Pna2<sub>1</sub>, a=10.3 b=8.2 c=5.0 Å

References:

<sup>1)</sup> I. S. Kerr (1974)

# Structure Type Index

Type species are marked by an asterisk. To make the index as informative as possible all reported species and designations have been included in this section, provided the structure type assignment appears reasonably well established. Even a number of occasionally used but discredited names of mineral species have been included in this index for the afore-mentioned reason. Moreover, the inclusion of a synthetic species designation in this index must not be interpreted to mean that the designation has been formally recognized or generally accepted but merely that the material has one of the established structure types. References have been restricted to those considered necessary to identify the species. For unreferenced minerals, see Strunz (1977).

* Afghanite	AFG	G. T. Wadlinger, E. J. Rosinski, and C. J. Plank (1968)
ALPHA	LTA	
A, Na-A	LTA	D. W. Breck, W. G. Eversole, R. M. Milton, T. B. Reed and T. L. Thomas (1956)
* Analcime	ANA	
- Analcite	ANA	
B	GIS	R. M. Milton (1961)
Ba-G	LTL	R. M. Barrer and D. J. Marshall (1964)
Ba-P	KFI	R. M. Barrer, L. Hinds and E. A. D. White (1953)
Ba-Q	KFI	R. M. Barrer, L. Hinds and E. A. D. White (1953)
Barrerite	STI	E. Passaglia and D. Pongiluppi (1975)
Basic cancrinite	CAN	R. M. Barrer and E. A. D. White (1952)
Basic sodalite	SOD	R. M. Barrer and E. A. D. White (1952)
* Bikitaite	BIK	
* Brewsterite	BRE	

1-D	ANA	L. L. Ames and L. B. Sand (1958)
incrinilite	CAN	
incrinilite hydrate	CAN	J. Wyart and Michel-Lévy (1949)
labazite	CHA	
inoptilolite	HEU	A. Alberti (1975)
ALSIO <sub>4</sub>	ABW	S. J. Chung and Th. Hahn (1972)
	CHA	D. W. Beck and N. A. Acara (1960)
1-Dardite	DAC	
anauite	SOD	
asimine	STI	
dingtonite	EDI	
pidessimine	STI	
plstilbite	EPI	
rionite	ERI	
aujasite	FAU	
errlerite	FER	
arronite	GIS	G. P. L. Walker (1962)
ilsmondine	GIS	
imelnite	GME	
ionnardite	THO	
l. otome	PHI	
ferschelilte	CHA	
leulandite	HEU	
hydroxysodalite	SOD	W. Borchert and J. Heidel (1947)
K, Ba) -G	LTL	R. M. Barrer and D. J. Marshall (1964)
	ANA	D. McConnell (1964)
Ceholite	EDI	R. M. Barrer and J. W. Baynham (1956)
ζ-F	MER	R. M. Barrer and J. W. Baynham (1956)
ζ-M		
Laubanite	NAT	
Laumontite	LAU	

Leonhardite	LAU	C. T. Amirov, V. V. Dyukhin and N. V. Belov (1987)
* Levyne	LEV	
Levynite	LEV	
* Li-A	ABW	R. M. Barrer and E. A. D. White (1951)
* Linde A	LTA	D. W. Breck, W. G. Eversole, R. M. Milton, T. B. Reed and T. L. Thomas (1958)
Linde B	GIS	R. M. Milton (1961)
Linde D	CHA	D. W. Breck and N. A. Acara '1980'
* Linde L	LTL	D. W. Breck (1965); D. W. Breck and E. M. Flanigen (1961)
Linde R	CHA	R. M. Milton (1960)
Linde T	OFF-ERI	D. W. Breck and N. A. Acara (1960)
Linde W	MER	R. M. Milton (1961)
Linde X	FAU	R. M. Milton (1959)
Linde Y	FAU	D. W. Breck (1964)
* Liottite	LIO	
* Losod	LOS	W. Sieber and W. M. Meier (1974)
* Mazzite	MAZ	
* Merlinoite	MER	
* Mordenite	MOR	
N-A	LTA	R. M. Barrer and P. J. Denny (1961)
Na-B	ANA	R. M. Barrer and E. A. D. W. 195
Na-D	MOR	R. M. Barrer and E. A. D. White (195)
Na-P1	GIS	R. M. Barrer, F. W. Bultitude and I. S. Kerr (1959)
Na-P2	GIS	R. M. Barrer, F. W. Bultitude and I. S. Kerr (1959)
* Natrolite	NAT	
Nosean	SOD	
O	OFF	R. Alello and R. M. Barrer (1970)
* Offretite	OFF	
Omega	MAZ	E. M. Flanigen (1968)

P-[Cr]	KFI	R. M. Barrer, L. Hinds and E. A. D. White (1953)
P <sub>2</sub> , P <sub>4</sub>	GIS	A. M. Taylor and R. Roy (1984)
Phillipsite	PHI	
P-L	LTL	E. M. Flanigen and R. W. Grose (1971)
P, Na-P	GIS	R. M. Barrer, J. W. Baynham, F. W. Bultitude, and W. M. Meier (1959)
Pollucite	ANA	
lolite	MOR	
Q-[Br]	KFI	R. M. Barrer, L. Hinds and E. A. D. White (1953)
R	CHA	R. M. Milton (1960)
RbAlSiO <sub>4</sub>	ABW	S. J. Chung and Th. Hahn (1972)
Rho	RHO	H. E. Robson, D. P. Shoemaker, R. A. Ogilvie and P. C. Manor (1973)
Scolecite	NAT	
S, Na-S	GME	R. M. Barrer, J. W. Baynham, F. W. Bultitude and W. M. Meier (1959)
Sodalite	SOD	
Sodalite hydrate	SOD	J. Wyart and M. Michel-Lévy (1949)
Sr-D	FER	R. M. Barrer and D. J. Marshall (1964)
Sr-Q	YUG	R. M. Barrer and D. J. Marshall (1964)
Stellerite	STI	
Stillbite	STI	
T	OFF-ERI	D. W. Breck and N. A. Acara (1960)
Tetracalcium trialuminate	SOD	V. I. Ponomarev, D. M. Khelker and N. V. Belov (1970)
Thomsonite	THO	
TMA-E	EAB	R. Aiello and R. M. Barrer (1970)
Tugtupite	SOD	H. Sorensen (1963)
Ultramarine	SOD	
Viselte	ANA	J. Mélon (1942)

W	MER	R. M. Milton (1961)
Walrakite	ANA	A. Steiner (1955)
Wellsite	PHI	P. Cerny, R. Rinaldi and R. C. Sdam (1977)
X	FAU	R. M. Milton (1959)
Y	FAU	D. W. Breck (1984)
* Yugawaralite	YUG	
Zeolon	MOR	
Zh	SOD	S. P. Zhdanov and N. N. Buntar (1959)
ZK-4	LTA	G. T. Kerr (1966)
* ZK-5	KFI	G. T. Kerr (1963)
ZK-19	PHI	G. H. Kuhl (1969)
ZK-20	LEV	G. T. Kerr (1969)
ZK-21	LTA	G. H. Kuhl (1967, 1971)
ZK-22	LTA	G. H. Kuhl (1967, 1971)
ZSM-4	MAZ	J. Ciric (1967)
* ZSM-5 <sup>1)</sup>	MFI	R. J. Argauer and G. R. Landolt (1972)
* ZSM-11	MEL	P. Chu (1973)

<sup>1)</sup> Recently, E. M. Flanigen et al (1978) reported a silica polymorph having the MFI structure type.

Exhibit C

## articles

**Silicalite, a new hydrophobic crystalline silica molecular sieve**

E. M. Flanigen, J. M. Bennett, R. W. Grose, J. P. Cohen, R. L. Patton & R. M. Kirchner  
Union Carbide Corporation, Tarrytown Technical Center, Tarrytown, New York 10591

J. V. Smith

Department of Geophysical Sciences, University of Chicago, Chicago, Illinois 60637

*A new polymorph of  $\text{SiO}_2$  (silicalite, refractive index 1.39, density  $1.76 \text{ g cm}^{-3}$ ) has a novel topologic type of tetrahedral framework. This encloses a three-dimensional system of intersecting channels defined by 10-rings wide enough to adsorb molecules up to 0.6 nm diameter. Silicalite is hydrophobic and organophilic, and selectively adsorbs organic molecules over water.*

A MAJOR scientific and technological achievement since 1949 has been the discovery and development of synthetic crystalline, aluminosilicate zeolites as molecular sieve adsorbents and catalysts. We now report the synthesis, crystal structure, and properties of silicalite, a new microporous crystalline silica with remarkable sieve properties. Unlike aluminosilicate zeolites which are hydrophilic, silicalite is hydrophobic and organophilic, and selectively adsorbs organic molecules in the presence of water.

The crystal structure is a new topologic type of tetrahedral framework, which contains a large fraction of five-membered

rings of silicon-oxygen tetrahedra. The framework outlines a three-dimensional system of intersecting channels defined by 10-rings of oxygen ions in all three directions. Organic quaternary ammonium ions which occupy the channels in the precursor obtained by hydrothermal synthesis, are removed by heating to yield silicalite. The resulting void occupies about 33% of the crystal volume, and the three-dimensional channel is wide enough to adsorb molecules up to about 6 Å in diameter. Silicalite can be heated to near 1,300 °C where it degrades to a glass.

**Synthesis**

The silicalite precursor is crystallized hydrothermally in a closed system containing alkylammonium cations (for example, tetrapropylammonium), hydroxyl ions, and a reactive form of silica at 100–200 °C. The organic-containing precursor crystals have a typical empirical composition  $(\text{TPA})_2\text{O} \cdot 48\text{SiO}_2 \cdot \text{H}_2\text{O}$ , mean refractive index 1.48, and measured density  $1.99 \text{ g cm}^{-3}$ . The organic cation is larger than the pore and therefore must be removed by chemical or thermal decomposition (usually calcination in air at 500–600 °C) to yield the microporous silicalite.

crystals (mean refractive index 1.39,  $\rho = 1.76 \text{ g cm}^{-3}$ ). As the silica framework is electrically neutral, the organic ion is apparently occluded with hydroxyl ions to maintain charge balance, as indicated by infrared spectroscopy. The unit cell composition for the precursor crystals can be expressed as  $[\text{4TPAOH} \cdot 96\text{SiO}_2]$ . Unlike aluminium-containing zeolites, silicalite has no cation exchange properties.

The crystallisation mechanism of the precursor seems to involve silica clathration of the hydrophobic organic cation analogous to the formation of crystalline water clathrates of alkylammonium salts<sup>1,2</sup>. Thus the silica tetrahedra assemble into a framework in place of the hydrogen-bonded water 'lattice' of the water clathrate, and surround the hydrophobic organic guest molecules. The alkylammonium ion seems to enhance the solubility of silica in water in a manner reminiscent of the 'structure-breaking' or 'cluster' forming properties of these same ions in aqueous solution<sup>3</sup>. Indeed, the alkylammonium ion further links the chemistry and structure of water and silica, and seems to translate the structural chemistry of water below room temperature to silica near 200 °C.

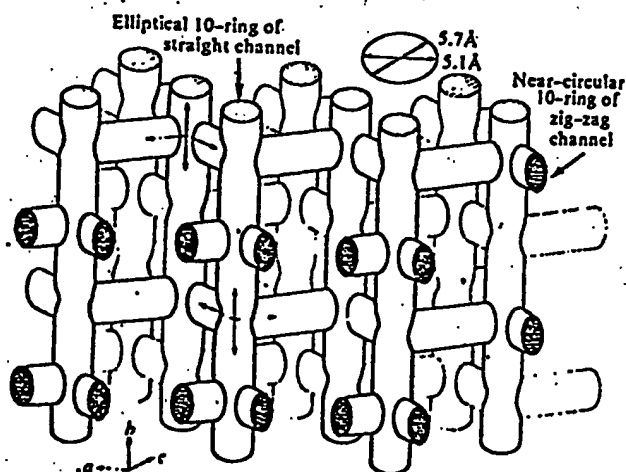
### Crystal structure

Precursor crystals are typically  $20 \times 20 \times 70 \mu\text{m}$  elongated along  $c$ , and commonly occur as interpenetrant twins on the (110) plane. Crystals calcined to 600 °C over 2 d have unit-cell edges  $a$ , 20.06;  $b$ , 19.80;  $c$ , 13.36 Å. The systematic absences ( $hk0$ ,  $h = 2n+1$ ;  $0k1$ ,  $k+1 = 2n+1$ ) indicate space group  $\text{Pnma}$  or  $\text{Pn}2_1a$ . Although the symmetry is apparently orthorhombic, weak diffractions may result from either lower symmetry or intergrowth of a second phase. From 8,297 diffraction intensities collected with monochromatised  $\text{CuK}\alpha$  radiation out to  $2\theta$  110° with a Picker FACS-1 diffractometer, 3,542 unique diffractions were obtained with 764 above background ( $3\sigma$ ). The crystal was twinned, and overlap of diffractions was corrected for the 90:10 ratio of the twin volumes.

Combination of direct methods (MULTAN program) and model building yielded the structure in  $\text{Pn}2_1a$  (Table 1). The 96 tetrahedra per unit cell form a 4-connected framework with a system of intersecting channels (Fig. 1) composed of near-circular zig-zag channels along  $a$  (free cross-section  $5.4 \pm 0.2$  Å) cross-linked by elliptical, straight channels along  $b$  (free cross-section  $5.7 \times 5.1 \times 5.2$  Å). Both channels are defined by 10-rings. The calculated free cross-section assumes that oxygen ions have a radius of 1.3 Å, and depends slightly on the choice of diametrically-opposing oxygens. The channel system same topology as that reported for a 'shape-selective' has the zeolite<sup>4</sup>, but structural details were not given.

Figure 2A is a photograph down the  $b$  axis of a model constructed from tetrahedral stars and plastic linkages. Figure

Fig. 1 Idealised channel system in silicalite. To avoid possible confusion caused by the perspective, the dimensions of the channels along  $c$  are shown at upper centre.



3A is a topological drawing showing how the framework can be constructed from pairs of tetrahedra, 4-rings and corrugated bands of 6-rings all cross-linked by 5-rings and occasional 6-rings. Figure 3B shows the  $a$ -axis projection. The corrugated bands of 6-rings are seen end-on, and each 4-ring lies between

Table 1 Atom positions in silicalite

Atom	x	y	z
Si (1)	0.4225 (6)	0.5468 (3)	0.3518 (9)
Si (2)	0.3055 (9)	0.5150 (10)	0.1943 (7)
Si (3)	0.1902 (2)	0.5570 (2)	0.3197 (6)
Si (4)	0.0687 (7)	0.5225 (8)	0.1616 (9)
Si (5)	0.2160 (8)	0.4223 (8)	0.4595 (10)
Si (6)	0.3752 (8)	0.4401 (10)	0.4627 (10)
Si (7)	0.0788 (8)	0.3597 (10)	0.1744 (10)
Si (8)	0.1888 (10)	0.3056 (10)	0.3060 (10)
Si (9)	0.3166 (10)	0.3582 (10)	0.1586 (10)
Si (10)	0.4266 (9)	0.3193 (10)	0.3227 (10)
Si (11)	0.1220 (10)	0.3138 (11)	0.9710 (10)
Si (12)	0.0754 (7)	0.1208 (8)	0.1912 (10)
Si (13)	0.1965 (9)	0.1517 (8)	0.3032 (10)
Si (14)	0.3187 (10)	0.1150 (10)	0.1766 (12)
Si (15)	0.4228 (10)	0.1631 (10)	0.3005 (12)
Si (16)	0.1184 (9)	0.1586 (10)	0.9420 (11)
Si (17)	0.2727 (8)	0.3166 (9)	0.9773 (11)
Si (18)	0.2752 (7)	0.1658 (9)	0.9599 (11)
Si (19)	0.2267 (9)	0.0492 (10)	0.4464 (11)
Si (20)	0.3845 (9)	0.0592 (8)	0.4818 (11)
Si (21)	0.4249 (8)	0.9393 (10)	0.3132 (12)
Si (22)	0.3063 (9)	0.9575 (10)	0.1701 (11)
Si (23)	0.1881 (9)	0.9450 (10)	0.3239 (12)
Si (24)	0.0590 (8)	0.9051 (8)	0.1989 (10)
O (1)	0.3834 (16)	0.3370 (17)	0.2262 (21)
O (2)	0.3730 (17)	0.5271 (18)	0.2454 (22)
O (3)	0.4837 (18)	0.5483 (17)	0.2972 (23)
O (4)	0.2409 (17)	0.5344 (18)	0.2262 (22)
O (5)	0.3047 (18)	0.4414 (19)	0.1849 (23)
O (6)	0.1082 (19)	0.5474 (18)	0.2573 (22)
O (7)	0.1234 (18)	0.3419 (19)	0.2806 (23)
O (8)	0.2527 (17)	0.3213 (18)	0.2209 (24)
O (9)	0.2995 (18)	0.3313 (17)	0.0822 (23)
O (10)	0.0963 (19)	0.3102 (18)	0.0572 (23)
O (11)	0.1306 (17)	0.1508 (19)	0.2555 (24)
O (12)	0.4967 (16)	0.1527 (17)	0.2721 (22)
O (13)	0.3214 (17)	0.0614 (18)	0.1352 (23)
O (14)	0.3687 (17)	0.1690 (18)	0.2261 (24)
O (15)	0.2481 (18)	0.1473 (16)	0.2212 (23)
O (16)	0.3214 (16)	0.1481 (18)	0.0394 (22)
O (17)	0.0836 (16)	0.4454 (19)	0.1702 (24)
O (18)	0.9931 (18)	0.3393 (18)	0.1904 (25)
O (19)	0.4274 (17)	0.2462 (19)	0.3529 (20)
O (20)	0.3866 (16)	0.4978 (18)	0.4116 (25)
O (21)	0.1827 (17)	0.4747 (18)	0.3853 (22)
O (22)	0.4039 (19)	0.3795 (18)	0.4059 (25)
O (23)	0.1907 (18)	0.3629 (18)	0.4021 (24)
O (24)	0.2892 (16)	0.4112 (17)	0.4760 (20)
O (25)	0.1802 (16)	0.4479 (18)	0.5685 (20)
O (26)	0.4021 (17)	0.4694 (16)	0.5966 (21)
O (27)	0.1974 (18)	0.2503 (18)	0.3459 (20)
O (28)	0.2054 (16)	0.3315 (16)	0.9469 (18)
O (29)	0.0696 (15)	0.3590 (16)	0.9334 (20)
O (30)	0.1011 (12)	0.2550 (16)	0.9533 (20)
O (31)	0.2768 (16)	0.2320 (18)	0.9137 (19)
O (32)	0.0818 (17)	0.1548 (17)	0.0798 (19)
O (33)	0.0766 (18)	0.0362 (18)	0.1714 (22)
O (34)	0.2074 (16)	0.1165 (18)	0.4281 (20)
O (35)	0.3970 (16)	0.1289 (16)	0.3892 (21)
O (36)	0.1917 (17)	0.1492 (17)	0.9844 (20)
O (37)	0.0959 (17)	0.1096 (16)	0.8882 (22)
O (38)	0.2978 (18)	0.3715 (17)	0.8828 (23)
O (39)	0.3030 (19)	0.1275 (16)	0.8621 (20)
O (40)	0.1989 (18)	0.0438 (17)	0.5593 (19)
O (41)	0.4144 (18)	0.0564 (17)	0.5818 (22)
O (42)	0.3853 (17)	0.9245 (18)	0.2291 (19)
O (43)	0.2588 (16)	0.9544 (18)	0.2675 (19)
O (44)	0.1171 (16)	0.9156 (17)	0.2414 (19)
O (45)	0.5020 (16)	0.9461 (17)	0.2986 (22)
O (46)	0.3103 (17)	0.0342 (16)	0.4894 (19)
O (47)	0.4198 (16)	0.9896 (17)	0.3833 (22)
O (48)	0.1992 (18)	0.9823 (17)	0.4196 (21)

Values in parentheses following the values for the atom parameters are the error values. The temperature factor was fixed at 1.0 for the silicon atoms and 2.5 for the oxygen atoms.

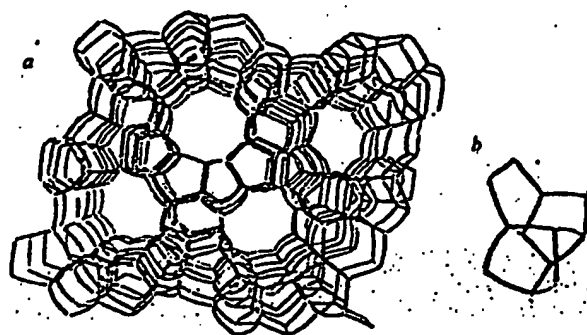
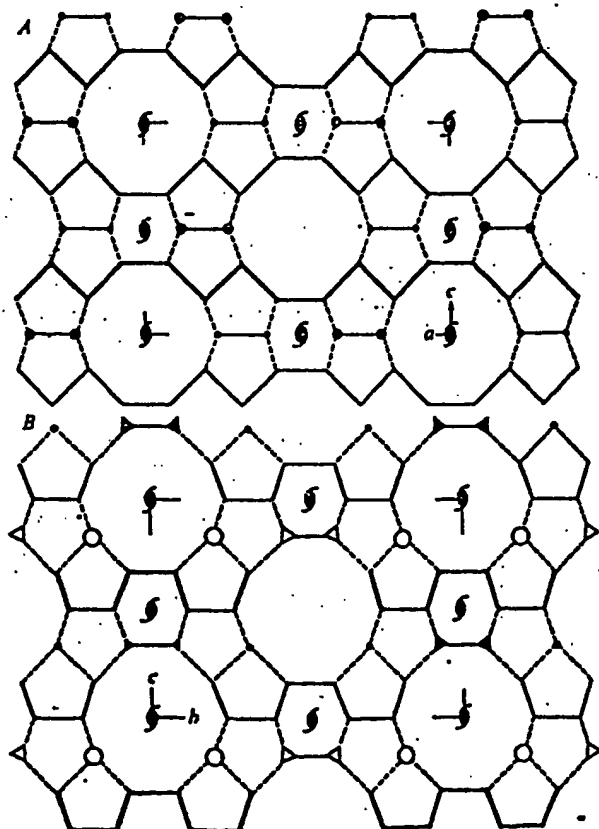


Fig. 2 A, Framework viewed down *b*; B, Secondary building unit of structure. Twelve tetrahedra linked into five 5-rings and one 6-ring.

two linked pairs. Particularly interesting is the high percentage of 5-rings, a feature shared with the zeolites dachiardite, mordenite, ferrierite and epistilbite. Two other polymorphs of silica, coesite and melanophlogite, also contain 5-rings. The frameworks of the zeolites listed above contain an infinite sheet of linked 6-rings, which might be regarded as a subunit involved in synthesis<sup>3,4</sup>. Perhaps the corrugated bands of 6-rings may be regarded as a sub-unit in the synthesis of silicalite. Alternatively, the silicalite structure can be assembled from subunits of 12 linked tetrahedra (Fig. 2B).

The structural subunits of silicalite can be assembled into other structure types, as will be described elsewhere. These theoretical frameworks give calculated X-ray powder patterns which do not match the observed X-ray powder pattern for

Fig. 3 Topologic drawings of silicalite structure. A, *b*-axis projection, B, *a*-axis projection. Si atoms lie at the intersections of the lines, and O atoms approximately half-way along the lines. Triple bands of corrugated 6-rings are shown by thick and thin continuous lines. Pairs of tetrahedra and 4-rings occur in projection in (B) as dots and circles and as linked open and filled triangles. In (A) the pairs of tetrahedra and the 4-rings superimpose as linked dots of two sizes. The corners of the unit cell are shown, together with screw diad axes of symmetry.



silicalite. The present structure gives a calculated pattern which fits well with the observed pattern (Fig. 4). Because of the weakness of intensities from the small crystal used for the structure determination, the *R* factor is rather high at 0.16. The twinning of silicalite around (110) may be due to faulting perpendicular to *b* allowing a pseudo-tetragonal framework that permits *a* and *b* axes to interchange giving the appearance of a (110) twin axis. An 'hourglass' zoning is also seen on the (010) and (100) faces. The calculated density is 1.80 g cm<sup>-3</sup> in good agreement with the measured 1.76 g cm<sup>-3</sup>.

### Adsorption

Silicalite is a molecular sieve adsorbent with an adsorption pore size near 6 Å and a saturation adsorption pore volume of 0.19 cm<sup>3</sup> g<sup>-1</sup> in agreement with the properties expected from its crystal structure. At ambient temperature, it adsorbs molecules as large as benzene (kinetic diameter 5.85 Å) but rejects molecules larger than 6 Å, such as neopentane (kinetic diameter 6.2 Å). Although the pore-size effect can be used in molecular sieving, its most remarkable adsorption property is surface selectivity. In contrast to the extremely high preference of aluminosilicate zeolite surfaces for water (hydrophilic) and other polar molecules, silicalite has a very low selectivity for the adsorption of water and a very high preference for the adsorption of organic molecules smaller than its limiting pore size. This hydrophobic and organophilic selectivity manifests itself in several ways. Adsorption of organic molecules and permanent gases on silicalite occurs by the volume filling of micropores as in zeolite molecular sieves and other microporous adsorbents. The filling of micropores occurs by physical adsorption at low relative pressures, and is characterised by enhancement of the adsorption energy due to increase of dispersion forces resulting from comparable size of the adsorption volume and the adsorbed molecule. This results in a type I, near rectilinear isotherm as illustrated for the gas phase adsorption of *n*-hexane on silicalite (Fig. 5b). Pore filling is essentially complete at a relative pressure of 0.03. In contrast, water does not fill the pores at any relative pressure (Fig. 5a). The adsorbed water volume at a relative pressure near one is about 25% of the saturation pore volume for *n*-hexane. In liquid or gaseous mixtures of organic molecules and water, silicalite selectively adsorbs the organic molecule, and thus is capable of removing organic molecules from organic-water streams.

Most solid surfaces are hydrophilic. Previously known hydrophobic surfaces<sup>7</sup> include graphitised carbon and microporous and macroporous silicas which have been rendered hydrophobic by removal of the hydrophilic surface hydroxyl groups either by thermal dehydration and dehydroxylation or by chemical modification of the surface to replace the hydroxyl

Table 2 Adsorption volumes in silicalite

Adsorbate	Temperature (°C)	Kinetic diameter (Å)	$V_p$ (cm <sup>3</sup> g <sup>-1</sup> )	$V_t$	Molecules adsorbed per unit cell
H <sub>2</sub> O	RT	2.65	0.047	0.083	15.1
O <sub>2</sub>	-183	3.46	0.185	0.326	38.0
CH <sub>3</sub> OH	RT	3.8	0.193	0.340	27.6
<i>n</i> -Butane	RT	4.3	0.190	0.334	10.9
<i>n</i> -Hexane	RT	4.3	0.199	0.350	8.8
SF <sub>6</sub>	RT	5.5	0.167*	—	10.9
C <sub>4</sub> H <sub>6</sub>	RT	5.85	0.134	0.236	8.7
Neo-pentane	RT	6.2	0.029	0.051	1.4

\*  $V_p$  (cm<sup>3</sup> g<sup>-1</sup>) = Total micropore volume in activated silicalite from saturation capacity, calculated using normal liquid densities at the adsorption temperature. Void fraction,  $V_t = V_p$  (cm<sup>3</sup> g<sup>-1</sup>) ×  $d_s$  (g cm<sup>-3</sup>), where  $d_s$  is the measured density 1.76 g cm<sup>-3</sup>. All samples activated by calcination in air at 600 °C followed by vacuum activation (10<sup>-3</sup> torr). Adsorption measurements all by gravimetric McBain-Baker balance technique. RT, room temperature.

\*At 760 torr.



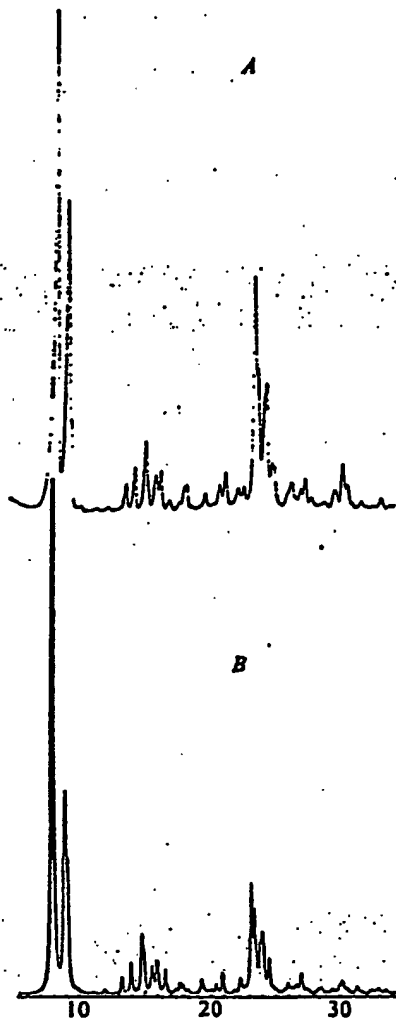


Fig. 4 X-ray powder diffraction pattern of *A*, calcined silicalite material, and *B*, calculated from parameters in Table 1. CuK $\alpha$  radiation with scale in degrees  $2\theta$ .

groups with hydrophobic organic or organosiloxane groups. The water isotherms (Fig. 5A) for Graphon, a dehydrated 'HiSil' silica, and a carbon molecular sieve with a pore size (5.0–5.5 Å) and pore volume (0.20 cm<sup>3</sup> g<sup>-1</sup>) comparable to that of silicalite, suggest that the silicalite surface is similar to or more hydrophobic than the Graphon and dehydrated HiSil surface. The carbon molecular sieve (commercial Pittsburgh activated carbon, Calgon Type MSC-V) is more hydrophilic.

The nature of a hydrophobic adsorbent surface has become understood within the last decade and is reviewed comprehensively in ref. 7. For physical adsorption on an ionic surface, the adsorption interaction energy consists of the sum of dispersion and repulsion energies which originate from non-specific interactions, and electrostatic polarisation, dipole and quadrupole energies which represent specific interactions. For adsorption of water, specific interactions are especially important. In the absence of surface sites which are 'hydrophilic', or of sites for hydrogen bonding, polar or acid-base interactions, the surface becomes nonspecific, homogeneous and hydrophobic. In water, each molecule is hydrogen-bonded to its neighbours (approximately four, as in ice), but in silicalite the narrowness of the channels allows interaction with only about two to three molecules on the average. Because silicalite is electrically neutral, there is no strong interaction with water molecules, and energetically the molecules prefer to remain as a liquid outside the silicalite. What small amount is adsorbed in silicalite is probably associated with the residual hydroxyl groups which persist after thermal removal of the

organic ion in the precursor. The initial isosteric heat of adsorption of water on silicalite is about 6 kcal mol<sup>-1</sup>, substantially below that of the heat of liquefaction of water (9.7 kcal mol<sup>-1</sup>), and similar to that reported for Graphon<sup>7</sup>. This requires a high entropy of adsorption, again like Graphon. Low energy and high entropy of adsorption (weak adsorption of highly entropic water) indicate high mobility of the adsorbed water molecule. The strongly hydrophilic nature of aluminosilicate zeolite molecular sieves is due to the presence in the intracrystalline void space of polar groups such as cations and hydroxyl groups, and field gradients generated by the substitution of aluminium for silicon in the tetrahedral framework. Silicalite has no aluminium and no cations in its structure. Chen<sup>8</sup> has shown a substantial decrease in the amount of water adsorbed on the zeolite mordenite (Zcolon) due to the removal of cations, as well as aluminium from the aluminosilicate framework,

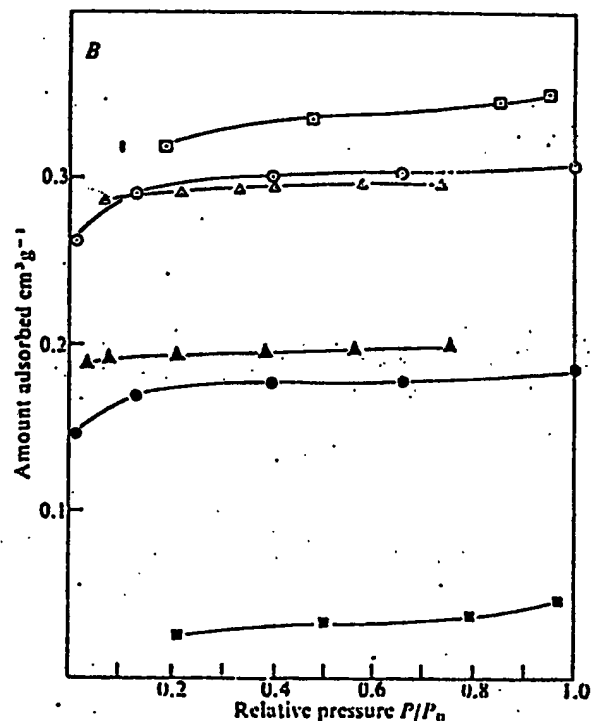
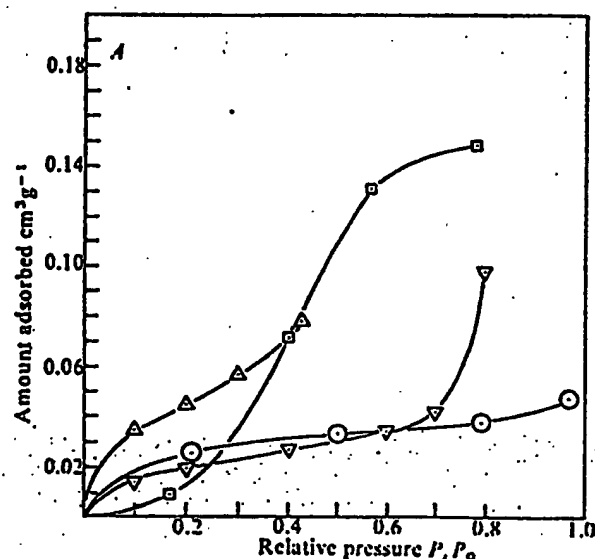


Fig. 5 *A* Water adsorption isotherms on hydrophobic surfaces.  $\square$ , Carbon molecular sieve;  $\Delta$ , Graphon;  $\nabla$ , HiSil;  $\circ$ , silicalite. *B*, Adsorption isotherms on silicalite and NaX zeolite.  $\circ$ ,  $\text{O}_2$  at  $-183^\circ\text{C}$ , samples activated at  $350^\circ\text{C}$ ,  $10^{-3}$  torr; McBain-Bakr gravimetric measurements.  $\square$ ,  $\text{H}_2\text{O}$  on NaX;  $\circ$ ,  $\text{O}_2$  on NaX;  $\Delta$ ,  $n$ -hexane on NaX;  $\Delta$ ,  $n$ -hexane on silicalite;  $\circ$ ,  $\text{O}_2$  on silicalite;  $\square$ ,  $\text{H}_2\text{O}$  on silicalite.

and described the resulting highly siliceous zeolites as 'hydrophobic'.

Adsorption of *n*-hexane in contrast is highly energetic with isosteric heats of adsorption of 16–18 kcal mol<sup>-1</sup> over a wide range of relative pressure. This range is substantially above the heat of liquefaction of *n*-hexane (7.8 kcal mol<sup>-1</sup>), and similar to the isosteric heat of adsorption of *n*-hexane on the molecular sieve zeolite X, again illustrating the high dispersion energy interactions in crystalline molecular sieves where the adsorption cavities and pores are  $\leq 10$  Å, commensurate with the size of the adsorbed molecule. Consideration of the volume, size and geometry of the void in the silicalite structure (Figs 1–3) and the number and size of *n*-hexane molecules (8.8 molecules per unit cell and 4.5 Å kinetic diameter) shows that the molecules must be highly oriented in nearly linear strings one molecule thick. The fit of *n*-hexane in the channels is near perfect, and *n*-hexane becomes a low entropy highly ordered liquid in the silicalite lattice. Typical adsorption volumes for a variety of molecules on silicalite are given in Table 2.

### Stability

Silicalite possesses a remarkable stability for a 33% porous crystal. It is stable in air to over 1,100 °C, and only slowly converts to an amorphous glass at 1,300 °C. It is stable to most mineral acids but reacts with HF similarly to quartz. X-ray emission measurements of the SiK $\beta$  band show that the mean Si–O bond energy of silicalite exceeds that of quartz by 0.1 eV,

and is essentially the same as for cristobalite. In contrast, the mean Si–O bond energy in aluminosilicate zeolites is substantially less than for quartz<sup>9</sup>.

### Applications

Thus silicalite may offer practical applications in the clean-up of water contaminated with organic compounds. Traces of methanol, propanol, butanol, phenol, 1,4-dioxane, pentane and hexane have been removed from water. The selectivity of silicalite is nearest to that of adsorbent carbons, but it has the advantage of much higher stability to regenerative commercial processes involving thermal, acid, and oxidative conditions.

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Exhibit D

*Hawley's*  
*Condensed Chemical*  
*Dictionary*

*TWELFTH EDITION*

*Revised by*  
Richard J. Lewis, Sr.



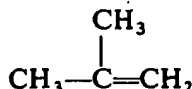
VAN NOSTRAND REINHOLD COMPANY  
New York

**isobutane hydrate.** See gas hydrates.

**isobutanol.** See isobutyl alcohol.

**isobutanolamine.** See 2-amino-2-methyl-1-propanol.

**isobutene.** (2-methylpropene; isobutylene).  
CAS: 115-11-7.  $(\text{CH}_3)_2\text{C}=\text{CH}_2$ . A liquefied petroleum gas.



**Properties:** Colorless, volatile liquid or easily liquefied gas. Coal-gas odor, bp  $-6.9^\circ\text{C}$ , fp  $-139^\circ\text{C}$ , flash p  $-105^\circ\text{F}$  ( $-76^\circ\text{C}$ ), d 0.6 (20C), soluble in organic solvents. Polymerizes easily and also reacts easily with numerous materials, autoign temperature  $869^\circ\text{F}$  ( $465^\circ\text{C}$ ).

**Derivation:** Fractionation of refinery gases, catalytic cracking of MTBE.

**Hazard:** Highly flammable, dangerous fire and explosion risk, explosive limits in air 1.8–8.8%.

**Use:** Production of isooctane, high-octane aviation gasoline, butyl rubber, polyisobutene resins, tert-butyl chloride, tert-butanol methacrylates; copolymer resins with butadiene, acrylonitrile, etc.; methyl-tert-butyl ether.

**isobutyl acetate.** CAS: 110-19-0.



**Properties:** Colorless, neutral liquid; fruit-like odor; soluble in alcohols, ether, and hydrocarbons; partially soluble in water. Bp  $116\text{--}117^\circ\text{C}$ , flash p  $64^\circ\text{F}$  ( $17.7^\circ\text{C}$ ) (CC), d 0.8685 (15C), refr index approximately 1.392, bulk d 7.23 lb/gal, fp  $-99^\circ\text{C}$ , autoign temp  $793^\circ\text{F}$  ( $422^\circ\text{C}$ ).

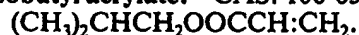
**Derivation:** Treating isobutanol with acetic acid in the presence of catalysts.

**Grade:** Technical, solvent, perfume, FCC.

**Hazard:** Flammable, dangerous fire risk. TLV: 150 ppm in air.

**Use:** Solvent for nitrocellulose; in thinners, sealants, and topcoat lacquers; perfumery; flavoring agent.

**isobutyl acrylate.** CAS: 106-63-8.



**Properties:** Liquid, bp  $61\text{--}63^\circ\text{C}$  (51 mm Hg), d 0.884 (25C), refr index 1.4124 (25C), flash p  $86^\circ\text{F}$  (30C) (TOC), contains 100 ppm monomethyl ether hydroquinone as inhibitor.

**Hazard:** Flammable, moderate fire risk.

**Use:** Monomer for acrylate resins.

**isobutyl alcohol.** (isopropylcarbinol; 2-methyl-1-propanol). CAS: 78-83-1.

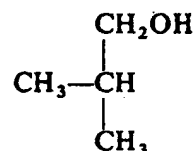


**Properties:** Colorless liquid, partially soluble in water, soluble in alcohol and ether, d 0.806 (15C), bp  $107^\circ\text{C}$ , flash p  $100^\circ\text{F}$  ( $37.7^\circ\text{C}$ ) (OC), fp  $-108^\circ\text{C}$ , refr index 1.397 (15C), autoign temperature  $800^\circ\text{F}$  ( $426^\circ\text{C}$ ).

**Derivation:** By-product of synthetic methanol production, purified by rectification.

**Hazard:** Flammable, moderate fire risk. Strong irritant. TLV: 50 ppm in air.

**Use:** Organic synthesis, latent solvent in paints and lacquers, intermediate for amino coating resins, substitute for n-butanol. Paint removers, fluorometric determinations, liquid chromatography, fruit flavor concentrates.



**isobutyl aldehyde.** See isobutyraldehyde.

**isobutylamine.** CAS: 78-81-9.



**Properties:** Colorless liquid, amine odor, strongly caustic, soluble in water, alcohol, ether, and hydrocarbons, d 0.731 (20C), boiling range  $66\text{--}69^\circ\text{C}$ , fp  $-85^\circ\text{C}$ , flash p  $15^\circ\text{F}$  ( $-9.4^\circ\text{C}$ ), autoign temperature  $712^\circ\text{F}$  ( $377^\circ\text{C}$ ).

**Hazard:** Flammable, dangerous fire risk. Strong irritant to skin and mucous membranes.

**Use:** Organic synthesis, insecticides.

**isobutyl-p-aminobenzoate.** CAS: 94-14-4.



**Properties:** White, crystalline scales; mp  $64\text{--}65^\circ\text{C}$ ; almost insoluble in water; soluble in alcohol, benzene, acetone.

**Use:** Medicine (topical anesthetic), sunscreen preparations.

**isobutylbenzene.** CAS: 538-93-2.



**Properties:** Liquid, d 0.8532 (20/4C), fp  $-51.6^\circ\text{C}$ , bp  $171.1^\circ\text{C}$ , refr index 1.486 (20C), flash p  $140^\circ\text{F}$  (60C), autoign temperature  $802^\circ\text{F}$  ( $427^\circ\text{C}$ ). Combustible.

**Hazard:** Moderate fire risk. Toxic in high concentration, a skin and eye irritant.

**isobutyl benzoate.** (eglantine).



**Properties:** Colorless liquid, characteristic odor, d 1.002, bp  $237^\circ\text{C}$ , insoluble in water, miscible with alcohol and ether. Combustible.

**Use:** Perfumes, flavors.

**isobutyl carbinol.** See isoamyl alcohol, primary.